

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification G:</b> <b>C08G 69/04, 69/08, 69/48, 69/44, 63/06, 63/685</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/26294</b> <b>(43) International Publication Date:</b> <b>24 July 1997 (24.07.97)</b>
<b>(21) International Application Number:</b> PCT/NL97/00015 <b>(22) International Filing Date:</b> 17 January 1997 (17.01.97) <b>(30) Priority Data:</b> 9600054 19 January 1996 (19.01.96) BE <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(73) Inventors/Applicants (for US only):</b> OUT, Gerardus, Jacobus, Joseph [NL/NL]; Wolcammersdreef 59C, NL-6216 RM Maastricht (NL). DE BRABANDER-VAN DEN BERG, Ellen, Marleen, Monique [NL/NL]; Provinciale weg Zuid 30, NL-6438 BE Schinnen (NL). NIJENHUIS, Atze, Jan [NL/NL]; Gangelstman 2, NL-6132 HB Sijard (NL). <b>(74) Agent:</b> VAN BOKHOVEN, Petrus, Hubertus, Maria; Oc- cennihuman DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, DE, GE, HU, IL, IS, JP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HIGHLY BRANCHED POLYMERS  <b>(57) Abstract</b> <p>The invention relates to a highly branched polymer containing chemically bound multifunctional monomer units represented by AQB<sub>x</sub>, in which Q represents a 1,3,5-triazine radical with nitrogens substituted at the 2, 4, 6 ring positions, A and B represent polymerizable functional groups which are linked to the triazine radical Q via the substituted nitrogens and which react during the polymerization, and x represents the number of B functional groups per said multifunctional monomer before polymerization and is greater than or equal to 2. The functional groups, A and B, react with each other, but not with themselves, under customary polymerization conditions, to form polymer linkages. The resulting highly branched polymer has a glass transition temperature between about 40 °C and about 300 °C and a weight-average molecular weight between about 10<sup>3</sup> and 10<sup>6</sup> g/mol.</p>		

BEST AVAILABLE COPY

WO 97/26294

PCT/NL97/00015

HIGHLY BRANCHED POLYMERS

## 5 BACKGROUND TO THE PRESENT INVENTION

1. Field of the Invention

The present invention relates to highly branched, uncrosslinked polymers prepared from multifunctional monomers having a structure represented by

10 AQB<sub>x</sub>. The present invention also relates to methods for the preparation of highly branched polymers and multifunctional monomers.

2. Description of Related Art

15 Nobel Laureate Paul J. Flory proposed highly branched soluble polymers which are not crosslinked but which have random branching in Journal of the American Chemical Society, 74, p. 2718 (1952). Flory's (theoretical) highly branched polymers are prepared by

20 polymerization of multifunctional monomers having a generic structure AB<sub>x</sub>, wherein A and B are functional groups and x is greater than or equal to 2. However, Flory's early proposal provides no guidance about how to impart advantageous properties to real commercially useful

25 polymers.

ICI's U.S. Patent No. 3,669,939 discloses the synthesis of highly branched, uncrosslinked aliphatic polyesters by polymerization of monomers each having one carboxylic acid functionality and a plurality of alcohol

30 functionalities. However, the low glass transition temperature (T<sub>g</sub>) of these polymers restricts their application temperature.

Professor Frechet and coworkers disclose the synthesis of highly branched, uncrosslinked polyesters or

35 polyamides in U.S. Patent No. 5,514,764, incorporated herein by reference. Aromatic monomers, A-R-B<sub>2</sub>, are employed wherein A and B represent functional groups which

WO 97/26294

- 2 -

PCT/NL97/00015

can form ester or amide linkages and R represents an aromatic unit. A drawback, however, is that these highly branched polymers have very high glass transition temperatures, which makes melt condensation and polymer processing difficult. Also, the starting monomers are water-sensitive and difficult to prepare.

The discovery of the present invention overcomes these and other problems associated with conventional highly branched polymers.

10

#### SUMMARY OF THE PRESENT INVENTION

Objects of the present invention include the preparation of highly branched polymers which have a glass transition temperature which allows for both a relatively high application temperature and melt processing. Another object is to use a monomer system having synthetic versatility, convenience, and stability. In addition, the properties of the polymer should be able to be tailored to allow the polymer to meet various applications.

20

These and other objects are achieved in the present invention for highly branched polymers containing chemically bound monomeric units represented by  $AQB_x$ , wherein Q represents a 1,3,5-triazine radical, A and B represent polymerizable functional groups linked to the triazine radical, and x represents the number of B groups per monomer unit and is greater than or equal to 2. The functional groups A and B can react with each other, but do not react with themselves, under customary polymerization conditions to form highly branched polymers containing triazine radicals in the highly branched polymer backbone. The properties of the polymer can be tailored by control of the structure of the functional groups. The polymers have glass transition temperatures between about 40°C and about 300°C, weight-average

30

WO 97/26294

- 3 -

PCT/NL97/00015

molecular weights between  $10^3$  and  $10^5$  g/mol, and contain rigid and flexible chain sections which allow for both sufficiently high application temperatures and desirable melt condensation and polymer processing behavior.

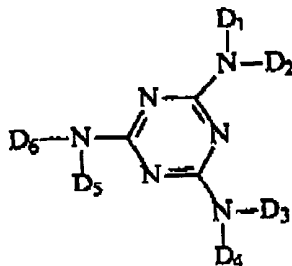
5 Advantages of the present invention include the diverse characteristics of these polymers which result from the diverse multifunctional monomers which can be readily prepared. For example, the functional groups A and B can contain alkyl segments which can be varied widely to  
10 tailor the polymer properties. Moreover, these highly branched polymers have better flame extinguishing characteristics compared to, for example, the aromatic, highly branched polymers disclosed in U.S. 5,514,764.

#### 15 DETAILED DESCRIPTION OF THE PRESENT INVENTION

The highly branched polymers according to the present invention contain at least 5 mol%, and preferably at least 10 mol%, and preferably at least 20 mol%, of  
20 polymerized multifunctional monomer  $AQB_x$ . If relatively dense polymers are required, then preferably more than 50 mol% of multifunctional monomer  $AQB_x$  is used.

The highly branched polymers can be, for example, highly branched polyesters, polyesteramides, polyamides, and polyurethanes. In particular, highly  
25 branched polyester, polyesteramide, and polyamide types of polymers are preferred.

In a preferred embodiment, the multifunctional monomer,  $AQB_x$ , can be represented by formula I:



WO 97/26294

- 4 -

PCT/NL97/00015

which illustrates the 1,3,5-triazine ring with nitrogen atoms substituted at the 2, 4, and 6 ring positions, with those nitrogen atoms having substituent groups, D<sup>1</sup> to D<sup>6</sup> attached. Each multifunctional monomer unit, AQB<sub>n</sub>, has one  
5 polymerizable functional A group, present in the D<sup>1</sup> group, and at least two polymerizable functional B groups, present in the D<sup>2</sup> to D<sup>6</sup> groups, as shown in formula I. Preferably, however, not all the D<sup>2</sup> to D<sup>6</sup> groups in  
10 formula I are functionalized with a B group. Thus, the preferred monomers contain both functionalized and unfunctionalized D groups linked to the triazine ring via the nitrogen atoms substituted at the 2, 4, and 6 ring positions.

The functionalized D<sup>1</sup> group can be represented  
15 by -X-A wherein X is a linking group between the nitrogen atom substituted onto the 1,3,5-triazine ring and A is the functional group which undergoes reaction during polymerization. Similarly, at least one of the D<sup>2</sup> to D<sup>6</sup> groups can be represented by -Y-B or -Y-B<sub>n</sub> if there is  
20 more than one B group bonded to Y, wherein Y is a linking group between the nitrogen atom substituted onto the 1,3,5-triazine ring and B is the functional group which also undergoes reaction during polymerization.

The X and Y linking groups can be identical or  
25 different and varied independently of each other. The X and Y linking groups can be, for example, a C1-C36 hydrocarbon group. In addition, the invention includes embodiments for X and Y wherein two hydrocarbon groups of the D-groups, substituted onto the same nitrogen atom, can  
30 form a heterocyclic ring. The heterocyclic ring includes the nitrogen atom bonded to the triazine ring at the 2, 4, or 6 ring position. Examples of heterocyclic groups include pyrrolidine and piperidine.

The C1-C36 hydrocarbon group can have a linear,

WO 97/26294

- 5 -

PCT/NL97/00015

branched or cyclic chain arrangement. The linear or branched chain structure can be saturated or unsaturated and can contain an alicyclic or aromatic compound. The hydrocarbon group can be, for example, derived from a C<sub>1</sub>-C<sub>36</sub>-alkane, a C<sub>3</sub>-C<sub>36</sub>-cycloalkane, a C<sub>2</sub>-C<sub>36</sub>-alkene, a C<sub>2</sub>-C<sub>36</sub>-alkyne, or C<sub>7</sub>-C<sub>36</sub>-arene. Examples include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, cyclopentane, hexane, cyclohexane, heptane, cycloheptane, octane, cyclooctane, decane, pentadecane, eicosane, docosane, triacontane, ethene, propene, butene, pentene, hexene, heptene, octene, nonene, decene, pentadecene, eicosene, docosene, triacontene, acetylene, propyne, butyne, pentyne, hexyne, heptyne, octyne, nonyne, decyne, pentadecyne, eicosyne, docosyne, triacontyne, benzene, toluene, xylene, ethylbenzene, n-propylbenzene, cumene, n-butylbenzene, isobutylbenzene, sec-butylbenzene, tert-butylbenzene, octylbenzene, tetradecylbenzene, eicosylbenzene.

Under customary polymerization conditions used by one skilled in the art, the functional groups A and B are generally reactive with each other, but in general, A will not react with A and B will not react with B (the functional groups A and B will not self react). Customary polymerization conditions are the conditions employed during melt or solution polymerization. The preferred polymerization conditions will depend on the functional groups and are known to those skilled in the art. For example, see Handbook of Polymer Synthesis, edited by Kricheldorf; Series: Plastic Engineering, 24 (1991), the complete disclosure of which is hereby incorporated by reference.

The D<sup>2</sup> to D<sup>6</sup> groups, are preferably not all functionalized to undergo polymerization. Unfunctionalized D groups can be, for example, independently of each other

WO 97/26294

- 6 -

PCT/NL97/00015

selected to be a hydrogen atom or a C1-C36 hydrocarbon group, or derivative thereof, as defined above for the linking groups X and Y. The unfunctionalized D group is preferably hydrogen because the multifunctional monomers  
5 are then simple to prepare.

The functional groups A and B can each include, for example, alcohol, ether, amine, alkylamine, carboxyl, oxycarbonyl, amide, hydroxyalkylamide, etheralkylamide, isocyanate, and acyl halide groups. The functional groups,  
10 for example, can be represented by  $-OR^1$ ,  $-NHR^1$ ,  $-COOR^1$ ,  $CONHR^1$ ,  $CONH-2-OR^1$ ,  $-NCO$ , or  $-COE$ , wherein E is a halogen such as fluoro, chloro, bromo, or iodo, and wherein  $R^1$  can be a hydrogen or a C1-C36 hydrocarbon group, and wherein Z can also be a C1-C36 hydrocarbon group. Preferably, the  
15 halogen E is chloro. In particular, alcohol, ether, amine, alkylamine, carboxyl, oxycarbonyl, amide, and hydroxyalkylamide groups are preferred because they can be incorporated into the multifunctional monomers in a simple and highly controlled fashion.

20 If the functional group A or B is a hydroxy-alkylamide group, Z represents a linkage between the hydroxyl and the amide groups. Similarly, if the functional group A or B is an etheralkylamide group, Z represents a linkage between the ether and amide groups.

25 The group  $R^1$  can be a hydrogen atom or a hydrocarbon group. The size and length of  $R^1$  is important insofar as it partly determines the reactivity of the functional groups.

The functional groups A and B are preferably  
30 present as terminal groups on the linking groups X and Y so that the functional groups are readily accessible and little steric hindrance is encountered in the polymerization reaction.

The number of functional groups B in each

WO 97/26294

- 7 -

PCT/NL97/00015

monomer unit, represented by x, is at least equal to 2. Preferably, x is smaller than 5, and preferably x is equal to 2. Preferably, three of the D groups in the monomer repeat unit remain unfunctionalized.

5 If a single D group contains more than one B functional group, n is in general equal to 2 or 3. Most preferably, however, n is equal to 1 (a single D group contains a single functional group B), because the multifunctional monomers can then be tailored in a simple and  
10 highly controllable manner.

In a preferred embodiment, the highly branched polymers are prepared from multifunctional monomers wherein the D<sup>1</sup> contains a carboxyl group A, and the D<sup>2</sup> and D<sup>3</sup> groups each contain at least one B group which is  
15 preferably a hydroxyl, amino, or hydroxyalkylamide group. Alternatively, the multifunctional monomers are also preferred wherein the D<sup>1</sup> group preferably contains a hydroxyl, amino, or hydroxyalkylamide group A, and the D<sup>2</sup> and D<sup>3</sup> groups each contain at least one carboxyl group B.

20 The groups D<sup>1</sup> to D<sup>6</sup> of the multifunctional monomers are preferably linear or branched groups containing the polymerizable functional groups A or B. The linear groups are more preferred because the functional groups A and B encounter little steric hindrance during  
25 reaction. The length of the linear backbone chain in this case can vary within wide limits and can be, for example, between 2 and 36 carbon atoms, and preferably, between 2 and 18 carbon atoms.

After polymerization, the glass transition  
30 temperature of the highly branched polymer is preferably between about 40°C and about 300°C (as measured by differential scanning calorimetry with a heating rate of 20°C/min). The length of the alkyl segments present in the monomer are preferably chosen so that the T<sub>g</sub> of the highly



WO 97/26294

- 8 -

PCT/NL97/00015

branched polymers is between about 50°C and about 150°C, and in particular, between about 50°C and about 130°C. Preferably, the alkyl segments include C2 to C8 groups.

The weight-average molecular weight of the highly branched polymers can be, for example, greater than about  $10^3$  g/mol, and preferably, greater than about 1,500 g/mol, and more preferably greater than about 2,000 g/mol. The weight-average molecular weight is generally less than about  $10^6$  g/mol, and preferably less than about 500,000 g/mol, and more preferably less than about 300,000 g/mol. The intrinsic viscosity  $[\eta]$  of the highly branched polymers is generally greater than about 0.01 dl/g, and preferably, greater than about 0.03 dl/g, and more preferably greater than about 0.05 dl/g. Intrinsic viscosity is generally less than about 1 dl/g, and preferably less than about 0.9 dl/g, and more preferably, less than about 0.6 dl/g. Weight-average molecular weight and intrinsic viscosity can be measured in hexafluoroisopropanol by size-exclusion chromatography (SEC) using a differential viscosimeter detector in combination with a UV-VIS and IR detector.

The highly branched polymers can be homopolymers or copolymers. Copolymers can be prepared from two or more monomers represented by the formulae AQB and AQB<sub>x</sub>, wherein at least one monomer is represented by AQB<sub>x</sub>. For these copolymers, A, Q, B and x are as defined above. The monomer AQB contains one and only one functional group B. An illustrative example of an AQB monomer is amino-(C<sub>2</sub>-C<sub>3</sub>)<sub>x</sub>-alkanoic acid. Copolymers can contain, or be prepared from, between about 5 and about 99.9 mol% of AQB<sub>x</sub> monomer and between about 0.01 and about 95 mol% of AQB monomer, and preferably, between about 10 and about 99.9 mol% of AQB<sub>x</sub> monomer and between about 0.01 and about 90 mol% of AQB monomer, and more preferably, between about 20 and

WO 97/26294

- 9 -

PCT/NL97/00015

about 99.9 mol% of AQB<sub>x</sub> monomer and about 0.01 and about 80 mol% of AQB monomer.

In addition, the highly branched polymer's molecular weight and molecular weight distribution can be controlled with the use of a compound which, for example, contains at least one functional group B, as defined above, but has no functional group A.

For a branched polymer prepared entirely from AQB<sub>x</sub> monomers, the degree of branching (DB) can be defined as the fraction of terminal groups (T) and branched groups (B) incorporated into the polymer with respect to the total number of monomers incorporated into the polymer, according to the following formula:

$$DB = (B + T) / (B + T + L)$$

wherein B represents the number of branching units where the functional group A and both functional groups B have reacted, T represents the number of terminal units where the A group but none of the B groups has reacted, and L represents the linear units where the A group and one of the B groups has reacted. It follows from the formula that for branched polymers of multifunctional monomers AQB<sub>x</sub>, the DB is between 0 and 1. The percentage of branching is equal to DB × 100.

The highly branched polymers of multifunctional monomers AQB<sub>x</sub> according to the invention have a percentage of branching of at least 40 %, and preferably, at least 50 %.

The highly branched polymers can be prepared using customary preparation methods for converting monomers with corresponding reactive groups into linear polymers. For example, condensation polymerization can be effected in the melt or in the presence of a solvent,

WO 97/26294

- 10 -

PCT/NL97/00015

including solution polymerization. A possible drawback of solvent-based polymerization, however, is that the solvent has to be removed again. Therefore, melt polymerization is preferred.

5 Polymerization catalysts can be employed to increase the rate of polymerization, and suitable catalysts are known to those skilled in the art. Catalysts for the preparation of polyesters, polyesteramides or polyamides include, for example, Brönsted and Lewis acids. 10 Examples include sulfonic acids such as, for example, methanesulfonic acid and p-toluenesulfonic acid; cobalt compounds such as, for example, cobalt(II) acetate; titanium compounds such as, for example, titanium(IV) (ethoxide)<sub>4</sub>, titanium(IV) (propoxide)<sub>4</sub>, titanium(IV) 15 (isopropoxide)<sub>4</sub>, titanium(IV) (butoxide)<sub>4</sub>, or titanium(IV) (2-ethylhexoxide)<sub>4</sub>; and tin compounds such as, for example, dibutyltin oxide, dibutyltin diacetate, dibutyltin bis(2-ethylhexanoate), and dibutyltin dilaurate. The amount of catalyst in the polymerization 20 mixture can vary from, for example, about 0.01 mol% to about 10 mol%, with respect to the molar amount of monomer and is preferably between about 0.2 and about 5 mol%. Most preferably, the amount is between about 0.5 mol% and about 2.5 mol%.

25 Polymerization can be effected at elevated temperature, and in general, can be between about 100°C and about 300°C. Polymerization temperature must not be so high as to give rise to decomposition or degradation of polymer or monomer, or unwanted cross-linking. Therefore, 30 polymerization temperature is preferably between about 140°C and about 280°C.

Polymerization pressure generally can be between about 10<sup>-6</sup> MPa and about 10<sup>-1</sup> MPa, and preferably, is between about 10<sup>-5</sup> MPa and 10<sup>-1</sup> MPa.

WO 97/26294

- 11 -

PCT/NL97/00015

During polymerization, the polymerization mixture changes usually from a thin liquid into a viscous paste. Glassy materials are generally obtained after cooling the mixture to room temperature,.

5           The highly branched polymers according to the present invention, in addition, can be modified with, for example, alkyl, aryl, and/or vinyl substituents in order to, for example, increase solubility in organic solvents, enhance compatibility with other polymers, crosslink the  
10 polymers, or tailor the Tg. Examples of reagents or substituents which can be used to modify the polymers include C<sub>1</sub>-C<sub>36</sub> alkanols, C<sub>1</sub>-C<sub>36</sub> alkanolic acids, N-hydroxyethyl-(C<sub>1</sub>-C<sub>36</sub>)-alkanoic amides, C<sub>1</sub>-C<sub>36</sub> alkanoyl chlorides, C<sub>1</sub>-C<sub>36</sub> alkyl isocyanates, C<sub>1</sub>-C<sub>36</sub> alkanolic acid esters, C<sub>1</sub>-  
15 C<sub>36</sub> alkylene oxides. In addition, aromatic and unsaturated compounds or substituents can be used such as, for example, phenols or acrylates respectively.

          The polymerization reactions are preferably carried out in a batch reactor vessel, but can also be  
20 carried out in a continuous or a semicontinuous process.

          Monomer preparation can be carried out by means of customary methods employed in the preparation of substituted 1,3,5-triazine derivatives. Such methods can entail, for example, nucleophilic substitution of cyanuric  
25 chloride which has three chlorine atoms of different reactivity. Exemplary methods are disclosed in, for example, Quirke, J.M.E., 1,3,5-Triazines, Comprehensive Heterocyclic Chemistry, Vol. 3, p. 482-485, Pergamon Press (1984), the complete disclosure of which is hereby  
30 incorporated by reference. Monomers can be prepared by reaction of cyanuric chloride with primary amines, H<sub>2</sub>NR, or secondary amines, HNRR', in the presence of sodium hydroxide. The amine substituents, R and R', are selected according to the desired configuration of the D<sup>1</sup> to D<sup>6</sup>

WU 97/26294

- 12 -

PCT/NL97/00015

groups, as defined above. The reaction medium can be an aqueous solution. Advantageously, the triazine's different chlorine atoms are reactive at different temperatures which allows the substituents to be varied. The reaction mixture in general should not be heated stepwise, but rather, should be heated only slowly, to prevent such problems as premature hydrolytic cleavage of chlorine atoms of cyanuric chloride and formation of cyanuric acid derivatives.

During monomer synthesis, when it is desired that one or more of the functional groups, A and B, be an amine or alkylamine group, an excess of  $H_2NR$  or  $HNRR'$  is preferably used. The excess amine helps prevent formation of branched products in which a plurality of 1,3,5-triazine rings are linked to one another via one or more diamino- $(C_2-C_{36})$ -alkane bridges.

In general, the monomers can be purified, for example, by acidifying the reaction mixture, which is preferably aqueous, to about pH 2 to 6. The monomer precipitates from solution and can be filtered off. If the multifunctional monomer is water-soluble, the metal salt of the monomer can be isolated by extraction. Preferably, the metal is an alkali metal such as, for example, sodium. Extraction can be carried out with various organic solvents such as, for example, tetrahydrofuran or acetone. Impurities are extracted and the metal salt is then dissolved in water. The aqueous solution is then acidified with a solution of a strong acid such as, for example, HCl or  $H_2SO_4$ . Water is subsequently evaporated, purified monomer is then extracted with organic solvent, and the solvent removed by evaporation.

The purity of the monomer can be checked by  $^1H$  NMR,  $^{13}C$  NMR,  $^{15}N$  NMR, elemental, and capillary electrophoresis analyses. In addition, terminal group

WO 97/26294

- 13 -

PCT/NL97/00015

determination via, for example, titration can be used. The purity is generally more than about 95 wt. %.

The presently disclosed highly branched polymers can serve, for example, as multifunctional crosslinkers in resins and coatings, multifunctional cores in star polymers, compatibilizers in polymer blends, melt elasticity enhancers, viscosity regulators, binders, adhesives, solubilizers, nucleants with respect to crystallization processes, ion exchangers, complexing agents, excipients of medicaments, catalysts, colorants, peroxides and other low molecular weight substances which are adsorbed on the surface or dispersed in the polymers.

The invention is further illustrated in the following non-limiting examples.

15

#### EXAMPLES

##### Example I: Monomer Preparation

2,4-bis( $\epsilon$ -carboxy-*n*-pentylamino)-6-(4-amino-*n*-butylamino)-*s*-triazine

20 To a suspension of 73.8 g (0.4 mol) of cyanuric chloride in 400 ml of water/ice, a solution of 104.9 g (0.8 mol) of 6-aminocaproic acid and 64 g (1.6 mol) of NaOH in 700 ml of water was added dropwise over a period of 1 h at 0°C. The reaction mixture was stirred for an additional 1 h at 0°C, after which an additional 500 ml of water were added. Over a period of 2 h, the mixture was warmed to 45°C, at which temperature stirring was continued for an additional 2 h. The reaction mixture was transferred into a dropping funnel, and over a period of 2 h, added dropwise to a mixture of 350 g (3.970 mmol) of 1,4-diaminobutane and 100 ml of 4M NaOH, which was stirred at 100°C. After addition was complete, stirring was continued for an additional 1 h at 100°C, after which the mixture was acidified with dilute H<sub>2</sub>SO<sub>4</sub> to pH 4 to 5. The

25

30

WO 97/26294

- 14 -

PCT/NL97/00015

white suspension which formed was filtered off and was further purified by recrystallization from water. Yield: 160 g (94 %); melting point: 140-145°C.

5 Example II: Monomer Preparation

2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(6-amino-n-hexylamino)-s-triazine

To a suspension of 73.8 g (0.4 mol) of cyanuric chloride in 600 ml of water/ice, a solution of 104.9 g (0.8 mol) of 6-aminocaproic acid and 64 g (1.6 mol) of NaOH in 1,000 ml of water was added dropwise over a period of 1.5 h. The reaction mixture was then stirred for an additional 1 h at 0°C. Over a period of 2 h, the mixture was warmed to 45°C, at which temperature the mixture was stirred for an additional 2 h. The mixture was then transferred to a dropping funnel, and over a period of 0.5 h, added to 464 g (4 mol) of 1,6-diaminohexane, which meanwhile was being heated from 50°C to 100°C. After complete addition, stirring was continued for a further 2 h at 100°C. After cooling to room temperature, the light suspension was filtered, and the filtrate was acidified with 37 % strength HCl to pH 4 to 5. The white suspension which formed was filtered off and recrystallized twice from 1,500 ml of water. Yield: 153 g (84 %); melting point: 175-180°C.

30 Example III: Monomer Preparation

2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamido-n-pentylamino)-s-triazine

To a suspension of 36.9 g (0.2 mol) of cyanuric chloride in 320 ml of water/ice, half of a solution of 52.5 g (0.4 mol) of 6-aminocaproic acid and 32 g (0.8 mol) of NaOH in 200 ml of water was added dropwise at 0-5°C (solution A). The reaction mixture was stirred for 2 h at

WO 97/26294

- 15 -

PCT/NL97/00015

0°C and then warmed to 40°C. The second half of solution A was added dropwise, over a period of 1h, after which stirring was continued for a further 2 h at 40-50°C. The reaction mixture was then heated to 80°C, and in four portions, a total of 50 ml of 4M NaOH and 34.85 g (0.2 mol) of (2-hydroxyethyl)-6-aminohexanecarboxylamide in 150 ml of water were added. After complete addition, the reaction mixture was stirred for a further 1.5 h at 100°C at pH 10. The mixture was then acidified to pH 3 by means of 50 % strength H<sub>2</sub>SO<sub>4</sub>, and the precipitate which formed was filtered off. The mother liquor was boiled down and filtered again. The combined residue fractions were recrystallized from a mixture of water and alcohol (40/60 % v/v). Melting point: 150-152°C.

15

Example IV: Monomer Preparation

2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamino)-s-triazine

To a suspension of 36.9 g (0.2 mol) of cyanuric chloride in 120 ml of ice/water, a solution of 52.5 g (0.4 mol) of 6-aminocaproic acid and 33 g (0.83 mol) of NaOH in 300 ml of water was added dropwise at 0-5°C. The reaction mixture was stirred for 1 h at 0°C and then for 2 h at 50°C. A solution of 18 g (0.3 mol) of ethanolamine and 8 g (0.2 mol) of NaOH in 40 ml of water was then added dropwise. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the mixture was filtered and acidified with 10 % strength H<sub>2</sub>SO<sub>4</sub> solution to pH 4. The precipitate which formed was filtered, washed with water and ethanol, dried and then recrystallized from 10 % of acetic acid/water. Yield: 60 g (75 %); melting point: 172-174°C.



WO 97/26294

- 16 -

PCT/NL97/00015

Example V: Monomer Preparation

2-( $\epsilon$ -carboxy-n-pentylamino)-4,6-bis-( $\beta$ -hydroxyethylamino)-s-triazine

A suspension of 75 g (0.41 mol) of cyanuric chloride in 225 ml of warm acetone was slowly added dropwise to 300 ml of ice/water. To this mixture, over a period of 10 minutes, 2 equivalents, 49.5 g (0.81 mol) of ethanolamine were added dropwise, the temperature of the reaction mixture rising from 8 to 22°C. Over a period of 5 hours, a solution of 33 g (0.83 mol) of NaOH in 300 ml of water was then added dropwise so that the pH of the reaction mixture remained below pH 7. The reaction mixture was then stirred for another 16 h at room temperature. The precipitate was filtered off, washed with water, and resuspended in 600 ml of water. Then 48.6 g (0.37 mol) of 6-aminocaproic acid were added, and the mixture was heated to 90°C. A solution of 33 g (0.83 mol) of NaOH in 300 ml of water was added dropwise over a period of 1 h. The reaction mixture was refluxed for 3 h, cooled to room temperature, and filtered. The filtrate was acidified with 300 ml of 1M H<sub>2</sub>SO<sub>4</sub> to pH 7 and then to pH 3 with 120 ml of 25 % strength KHSO<sub>4</sub> solution. The water was evaporated and Na<sub>2</sub>SO<sub>4</sub> was added to the residue. The mixture was then extracted with acetone by soxhlet extraction. Finally, the extract was boiled down. Yield: 99 g (74 %)

Example VI: Polymer Preparation

Preparation of polyamide from 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(4-amino-n-butylamino)-s-triazine

A quantity of 30 g of 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(4-amino-n-butylamino)-s-triazine was degassed five times, aerated with N<sub>2</sub>, and then, heated at 175°C under a vacuum of 0.5 Pa for 8 h in a rotary evaporator which was heated with the aid of an oil bath.

WO 97/26294

- 17 -

PCT/NL97/00015

During the polymerization water was liberated, and the initially thin melt changed into a highly viscous paste. After cooling, 28 g of pale-yellow glassy material was obtained.  $T_g$ : 88°C.  $M_v$ : 20,000 g/mol,  $M_w/M_n$ : 10,  $[\eta]$ : 0.15 dl/g (hexafluoroisopropanol, room temperature RT).

Example VII: Polymer Preparation

Preparation of polyester from 2-( $\epsilon$ -carboxy-n-pentylamino)-4,6-bis-( $\beta$ -hydroxyethylamino)-s-triazine

10 A quantity of 12.5 g of 2-( $\epsilon$ -carboxy-n-pentylamino)-4,6-bis-( $\beta$ -hydroxyethylamino)-s-triazine and 95 mg of dibutyltin oxide was degassed five times, aerated with  $N_2$ , and then heated at 190°C under a vacuum of 0.5 Pa for 8 h in the abovementioned rotary evaporator. During  
15 the polymerization, water was liberated, and the thin melt changed into a highly viscous paste. After cooling, 10.5 g of glassy yellow-orange polymer was obtained.  $T_g$ : 103°C.  $M_v$ : 7,200 g/mol,  $M_w/M_n$ : 3.5,  $[\eta]$ : 0.09 dl/g (hexafluoroisopropanol, RT).

20

Example VIII: Polymer Preparation

Preparation of polyesteramide from 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamido-n-pentylamino)-s-triazine

25 A quantity of 4.8 g of 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamido-n-pentylamino)-s-triazine and 24 mg of dibutyltin oxide was degassed, aerated with  $N_2$ , and then heated at 190°C under 0.2 Pa for 7.5 h in the abovementioned rotary evaporator. During  
30 polymerization, water was liberated, and the thin melt changed into a highly viscous paste. After cooling, 4.7 g of polymer was obtained.  $T_g$ : 61°C.  $M_v$ : 106,000 g/mol,  $M_w/M_n$ : 96,  $[\eta]$ : 0.20 dl/g (hexafluoroisopropanol, RT).

WO 97/26294

- 18 -

PCT/NL97/00015

**Example IX: Polymer Preparation**

Preparation of copolyamide from 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(4-amino-n-butylamino)-s-triazine and 6-aminocaproic acid

- 5 A quantity of 2.6 g of 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(4-amino-n-butylamino)-s-triazine and 2.4 g of 6-aminocaproic acid was degassed five times, aerated with N<sub>2</sub> and then heated at 190°C under 0.1-1.5 Pa for 6 h in the abovementioned rotary evaporator. During  
10 polymerization, water was liberated, and the thin melt changed into a highly viscous paste. After cooling, 3.95 g of glassy pale yellow polymer was obtained.  $M_w$ : 62,000 g/mol,  $M_w/M_n$ : 22,  $[\eta]$ : 0.27 dl/g (hexafluoroisopropanol, RT).

15

**Example X: Polymer Preparation**

Preparation of polyester from 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamino)-s-triazine

- A quantity of 5.02 g of 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-( $\beta$ -hydroxyethylamino)-s-triazine and 50 mg  
20 of methanesulfonic acid was heated for 6 h at 185°C, followed by postcondensation at 220°C for 1.5 h. The resulting pale brown glassy polymer was ground and added to a solution of thionyl chloride in tetrahydrofuran.  
25 Under reflux, the polymer slowly dissolved, the terminal carboxyl groups being converted into acyl chloride groups. The solution was boiled down and then dissolved in absolute tetrahydrofuran to which triethylamine had been added. An excess of absolute ethanol was then added  
30 dropwise. The polymer solution was precipitated in a tetrahydrofuran/water mixture, and the polymer dried under vacuum.  $M_w$ : 42,000 g/mol,  $M_w/M_n$ : 12,  $[\eta]$ : 0.08 dl/g (hexafluoroisopropanol, RT).

WO 97/26294

- 19 -

PCT/NL97/00015

Example XI: Polymer Preparation

Preparation of polyamide from 2,4-bis( $\epsilon$ -carboxy-n-pentyl-amino)-6-(6-amino-n-hexylamino)-s-triazine

A quantity of 65 g of 2,4-bis( $\epsilon$ -carboxy-n-pentylamino)-6-(6-amino-n-hexylamino)-1,3,5-triazine was degassed ten times, aerated with  $N_2$ , and then heated at 175°C under 0.1 Pa for 6 h in a rotary evaporator which was heated with the aid of an oil bath. The pressure was then reduced to a vacuum of 0.15 Pa and heating continued for a further 25 h. During the polymerization, water was liberated, and the viscous melt changed into a highly viscous paste. After cooling, 62.5 g of pale yellow glassy material was obtained.  $T_g$ : 79°C.  $M_v$ : 139,000 g/mol,  $M_w/M_n$ : 10,  $[\eta]$ : 0.44 dl/g (hexafluoroisopropanol, RT).

While the present invention has been disclosed in detail and with reference to specific embodiments thereof, it will be apparent to those of ordinary skill in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

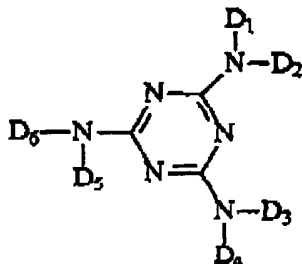
WO 97/26294

- 20 -

PCT/NL97/00015

CLAIMS

1. A composition comprising a branched polymer containing chemically bound multifunctional monomer units of the formula  $AQB_x$ , wherein,
- 5 (i) Q represents a 1,3,5-triazine radical, A and B represent polymerizable functional groups linked to said triazine radical Q which react during said polymerization, and x represents the number of B functional groups per said
- 10 multifunctional monomer before said polymerization and is greater than or equal to 2,
- (ii) said functional groups, A and B, react with each other, but not with themselves, under
- 15 customary polymerization conditions,
- (iii) said functional groups A and B react to form linkages, and
- (iv) said branched polymer has a glass transition
- 20 temperature between about 40°C and about 300°C and a weight-average molecular weight between about  $10^3$  and  $10^6$  g/mol.
2. A composition according to claim 1, wherein said multifunctional monomer,  $AQB_x$ , is represented by
- 25 formula I:



WO 97/26294

- 21 -

PCT/NL97/00015

- 5 said polymerizable functional group A is contained within the D<sup>1</sup> group, said polymerizable functional groups B are contained within the D<sup>2</sup> to D<sup>6</sup> groups, and said functional groups A and B are selected from the group consisting of -OR<sup>1</sup>, -NHR<sup>1</sup>, -COOR<sup>1</sup>, CONHR<sup>1</sup>,  
10 CONH-Z-OR<sup>1</sup>, -NCO, or -COE, wherein E is halogen. R<sup>1</sup> can be hydrogen or a C1 to C36 hydrocarbon group, and Z can be a C1 to C36 hydrocarbon group.
- 15 3. A composition according to claim 2, wherein said D<sup>1</sup> is represented by -X-A, at least one of said D<sup>2</sup> to D<sup>6</sup> groups are represented by -Y-B<sub>n</sub>, X and Y can be C1 to C36 hydrocarbon groups, n is 1, 2, or 3, and X and Y link A and B, respectively, to the nitrogen atoms substituted onto the 1,3,5-triazine ring.
- 20 4. A composition according to claim 3, wherein n is 1.  
5. A composition according to claim 3, wherein X and Y are C1 to C36 hydrocarbon groups derived from a hydrocarbon group selected from the group consisting of C<sub>1</sub> to C<sub>36</sub>-alkanes, C<sub>1</sub> to C<sub>36</sub>-cycloalkanes, C<sub>2</sub> to C<sub>36</sub>-alkenes, C<sub>2</sub> to C<sub>36</sub>-alkynes, and C<sub>7</sub> to C<sub>36</sub>-arenes.
- 25 6. A composition according to claim 3, wherein the two hydrocarbon groups of the D-groups substituted onto the same nitrogen atom forms a heterocyclic ring, in which the heterocyclic ring includes the nitrogen atom bonded to the triazine ring at the 2, 4 or 6 ring position.
- 30 7. A composition according to claim 5, wherein X and Y are selected from the group consisting of methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, cyclopentane, hexane, cyclohexane, heptane, cycloheptane, octane, cyclooctane, decane, pentadecane, eicosane, docosane, triacontane, ethene, propene, butene, pentene, hexene, heptene, octene, nonene, decene, pentadecene,

WO 97/26294

- 22 -

PCT/NL97/00015

- eicosene, docosene, triacontene, acetylene, propyne, butyne, pentyne, hexyne, heptyne, octyne, nonyno, decyne, pentadecyne, eicosyne, docosyne, triacontyne, benzene, toluene, xylene, ethylbenzene, n-propylbenzene, cumene, n-butylbenzene, isobutylbenzene, sec-butylbenzene, tert-butylbenzene, octylbenzene, tetradecylbenzene, and eicosylbenzene.
- 5
8. A composition according to claim 3, wherein the number of carbon atoms in the groups D<sup>1</sup> to D<sup>6</sup> is between about 2 and 8 carbon atoms.
- 10
9. A composition according to claim 3, wherein D<sup>2</sup>, D<sup>4</sup> and D<sup>6</sup> are hydrogen atoms.
- 10.
10. A composition according to claim 3, wherein D<sup>1</sup> contains a COOH group and D<sup>3</sup> and D<sup>5</sup> each contain at least one OH, NH<sub>2</sub> or CONH-Z-OH group.
- 15
11. A composition according to claim 3, wherein D<sup>3</sup> and D<sup>5</sup> each contain at least one COOH group and D<sup>1</sup> contains an OH, NH<sub>2</sub> or CONH-Z-OH group.
- 12.
- 20 A composition according to claim 1, wherein said highly branched polymer has a glass transition temperature between about 50°C and about 130°C.
- 13.
- 25 A composition according to claim 1, wherein said highly branched polymer also contains a compound having no functional group A and at least one functional group B.
- 14.
- 30 A composition according to claim 1, wherein said highly branched polymer has a degree of branching of at least 40 %.
- 15.
- 30 A composition according to claim 1, wherein said highly branched polymer is a polyester, a polyesteramide, or a polyamide.
- 16.
- A composition according to claim 1, wherein said highly branched polymer contains at least 5 mol % of multifunctional monomer unit, AQB<sub>x</sub>.

WO 97/26294

- 23 -

PCT/NL97/00015

17. A composition according to claim 1, wherein said highly branched polymer is a copolymer which contains about 0.01 to about 95 mol% of AQB monomer units and about 5 to about 99.9 mol% of AQB<sub>n</sub> monomer units.
- 5 18. A composition according to claim 17, wherein said highly branched polymer is a copolymer which contains about 10 to about 99.9 mol% of AQB monomer units and about 0.01 to about 90 mol% of AQB<sub>n</sub> monomer units.
- 10 19. A composition according to claim 18, wherein said highly branched polymer is a copolymer which contains about 20 to about 99.9 mol% of AQB monomer units and about 0.01 to about 80 mol% of AQB<sub>n</sub> monomer units.
- 15 20. A method for the preparation of a highly branched polymer according to claim 1, wherein said polymerization occurs in a melt at a temperature between about 140 and 280°C.
21. A method according to claim 20, wherein polymerization catalysts are employed in the melt.
- 20 22. The use of a highly branched polymer according to claim 1, wherein said highly branched polymer is used as a multifunctional crosslinker in resins and coatings, multifunctional core for star polymers, compatibilizer in polymer blends, melt elasticity enhancers, viscosity regulators, binders, adhesives, 25 solubilizers, nucleants with respect to crystallization processes, ion exchangers, complexing agents, excipients of medicaments, catalysts, colourants, peroxides and other low molecular weight substances which are adsorbed on the surface or 30 dispersed in said polymers.
23. A composition comprising a multifunctional monomer of the formula AQB<sub>n</sub>, wherein,
- (i) Q represents a 1,3,5-triazine radical, A and B represent polymerizable functional groups



WO 97/26294

- 24 -

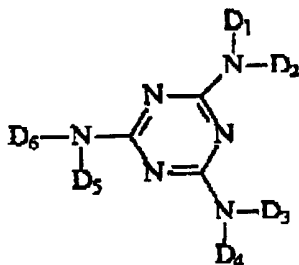
PCT/N1.97/00015

linked to said triazine radical Q which react during polymerization, and x represents the number of B functional groups per said multifunctional monomer before said polymerization and is greater than or equal to 2.

(ii) said functional groups, A and B, react with each other, but not with themselves, under customary polymerization conditions, and

(iii) said functional groups A and B react to form linkages.

24. A composition according to claim 23, wherein said multifunctional monomer,  $AQB_x$ , is represented by formula I:



said polymerizable functional group A is contained within the D<sup>1</sup> group, said polymerizable functional groups B are contained within the D<sup>2</sup> to D<sup>6</sup> groups, and said functional groups A and B are selected from the group consisting of -OR<sup>1</sup>, -NHR<sup>1</sup>, -COOR<sup>1</sup>, CONHR<sup>1</sup>, CONH-Z-OR<sup>1</sup>, -NCO, or -COE, wherein E is halogen, R<sup>1</sup> can be hydrogen or a C1 to C36 hydrocarbon group, and Z can be a C1 to C36 hydrocarbon group.

25. A composition according to claim 24, wherein said D<sup>1</sup> is represented by -X-A, at least one of said D<sup>2</sup> to D<sup>6</sup> groups are represented by -Y-B<sub>n</sub>, X and Y can be C1 to

WO 97/26294

- 25 -

PCT/NL97/00015

- C36 hydrocarbon groups, n is 1, 2, or 3, and X and Y link A and B, respectively, to the nitrogen atoms substituted onto the 1,3,5-triazine ring.
26. A composition according to claim 25, wherein n is 1.
- 5 27. A composition according to claim 25, wherein X and Y are C1 to C36 hydrocarbon groups derived from a hydrocarbon group selected from the group consisting of C<sub>1</sub> to C<sub>36</sub>-alkanes, C<sub>1</sub> to C<sub>36</sub>-cycloalkanes, C<sub>2</sub> to C<sub>36</sub>-alkenes, C<sub>2</sub> to C<sub>36</sub>-alkynes, and C<sub>7</sub> to C<sub>36</sub>-arenes.
- 10 28. A composition according to claim 27, wherein X and Y are two hydrocarbon groups substituted onto the same nitrogen atom to form a heterocyclic ring.
29. A method for the preparation of a multifunctional monomer according to claim 24, wherein cyanuric chloride is reacted with primary amines, H<sub>2</sub>NR, or
- 15 secondary amines, HNRR', in the presence of sodium hydroxide in an aqueous solution, and R and R' are selected according to the desired configuration of the D<sup>1</sup> to D<sup>6</sup> groups in the AQB<sub>n</sub> monomer.

## INTERNATIONAL SEARCH REPORT

In national Application No  
PCT/NL 97/00015

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G69/04 C08G69/08 C08G69/48 C08G69/44 C08G63/06  
C08G63/685

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92 08749 A (CORNELL RES FOUNDATION INC) 29 May 1992 cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

- \* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* "A" document member of the same patent family

Date of the actual completion of the international search

20 February 1997

Date of mailing of the international search report

12. 03. 97

Name and mailing address of the ISA

European Patent Office, P.O. Box 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2000, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Leroy, A

Form PCT/ISA/210 (second sheet) (July 1992)

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/NL 97/00015

Patent document cited in search report	Publication date	Patent family number(s)	Publication date
WO-A-9208749	29-05-92	CA-A- 2096144	20-05-92
		EP-A- 0558556	08-09-93
		JP-T- 6502442	17-03-94
		US-A- 5514764	07-05-96
-----			

Form PCT/ISA/210 (patent family annex) (July 1992)